

Title	Novel Solutions to New Problems in Paper Deinking
Type	Article
URL	http://ualresearchonline.arts.ac.uk/1503/
Date	2007
Citation	Fricker, Anna["lib/metafield:join_ualname" not defined]Manning, Andrew["lib/metafield:join_ualname" not defined]Thompson, Robert (2007) Novel Solutions to New Problems in Paper Deinking. Pigment and Resin Technology The international journal of colourants, polymers and colour applications, volume (number). pp. 141-152. ISSN 03699420
Creators	Fricker, Anna["lib/metafield:join_ualname" not defined]Manning, Andrew["lib/metafield:join_ualname" not defined]Thompson, Robert

Usage Guidelines

Please refer to usage guidelines at <http://ualresearchonline.arts.ac.uk/policies.html> or alternatively contact ualresearchonline@arts.ac.uk.

License: Creative Commons Attribution Non-commercial No Derivatives

Unless otherwise stated, copyright owned by the author

Novel solutions to new problems in paper deinking

A Fricker, R Thompson and A Manning

Abstract

This paper describes and evaluates the traditional methods for effective ink removal during the recycling of printed papers. Additionally novel techniques for dealing with the newer 'difficult to deink' inks such as toners from photocopiers, UV-cured ink films and liquid toner suspensions or Electroinks® were evaluated.

High intensity ultrasound was applied to pulps derived from papers printed with these newer inks in order to evaluate its effectiveness in detaching the inks from paper and establishing the resultant ink particle size distributions. When exposed to ultrasound at a frequency of 20 kHz it was found that 'difficult to deink' pulps did exhibit significant ink detachment. In the case of toners temperature did have an effect on particle breakdown with larger numbers of particles produced at temperatures well below the softening point which was attributed to a greater brittleness of the toner at lower temperatures. Electroinks® can be effectively de-inked by exposure to ultrasound coupled with washing under neutral conditions. With all the inks investigated exposure to ultrasound resulted in the detached ink having particle size distributions that can be removed by conventional flotation and washing techniques.

The exposure of the pulp to ultrasound was only carried out using a batch-wise process. A future development would be to use a continuous flow system incorporating an annular ultrasound horn. Introducing ultrasound exposure into a conventional deinking plant, all post-consumer printed waste paper could be deinked without the use of deinking chemicals. The findings are of interest to those in paper recycling

Introduction

There is a long tradition in Europe of producing paper from recycled materials. Between 1250AD and 1875AD paper was made utilising fibres reclaimed from flax, hemp and cotton. However from around 1860 virgin fibres derived from wood pulp were used. These cellulose fibres were obtained from both chemical and mechanical means. Since 1950 there has been an increasing utilisation of recycled wood fibres in both paper and board production.

The production of recycled newsprint began in the late 1960s with manufacturers using about 60% recycled fibre with 40% virgin fibre. Since that time the drive to use less of the expensive virgin fibre has resulted in newsprint being produced from 100% recycled fibre. In more recent years attention has turned to the use of recycled fibres in higher quality printing papers. Currently there are many examples of both coated and uncoated papers being manufactured that contain up to 80% recycled fibre.

In Europe legislation has been introduced that restricts the use of land fill sites, this coupled with increasing international requirements for greater recyclability of all products and ongoing concerns about the environment have all contributed to the demand for an increase in the recycling of wastepaper.

What is the definition of wastepaper?

Wastepaper is obtained from two sources, pre-consumer waste and post-consumer waste. Pre-consumer waste comes from over issues that are returned from the printer,

press-room waste and mill broke. Most of this waste has not been printed and this unprinted material is easy to repulp and reform into paper. Post-consumer waste is invariably contaminated with contraries that need to be separated out before repulping. Additionally the post-consumer waste will have been printed with a variety of inks and these inks will have to be removed before repulping.

If large particles of ink ($>40\mu\text{m}$) are not removed the pulp will produce papers that are blemished with visible specks of ink. However, if the ink particles are less than $40\mu\text{m}$ diameter in size the eye cannot resolve them so they will reduce the whiteness and brightness of the paper or add greyness.

The recycling process

Overall, the recycling process involves: repulping the wastepaper to reduce it to a fibre slurry; de-inking – separating ink from the cellulose fibres; and finally removal of the ink particles from the stock. The fibre slurry is then turned into paper using conventional papermaking machines (Thompson 2004).

The source of recyclable fibre has been mainly newsprint and magazine waste. It is important to have a suitable combination of both long and short fibre to yield a pulp that will produce paper of acceptable quality. Magazine waste provides some longer fibre material (chemical wood) which improves the overall quality to a newsprint (mechanical wood) furnish. The requirements for the quality of newsprints are now higher than ever before. They are required to run at speeds of up to $750\text{ metres min}^{-1}$ (70,000 copies per hour) with a web break incidence of less than 1%. A clean white sheet is required for process colour printing on both sides of the web and strong surface properties are necessary to minimise dusting and linting. Overall the papermaker is being asked to produce a more highly specified product. Pulp furnishes for the higher quality graphics papers rely on mixed office waste (photocopier paper and ink-jet printed papers).

As stated earlier the first stage in recycling wastepaper involves repulping to reduce the material to a fibre slurry. This defibring is achieved by stirring the waste in the presence of water and chemicals using a hydropulper. During this process fibres can be shortened as a result of breaking (cutting). The breaking of fibres is less likely to occur if the pulps are at a higher consistency as the action of fibre against fibre is gentler than fibre against metal pulper paddle. Ink detachment takes place simultaneously with defibring. The final task is to remove the separated ink particles from the stock.

Different techniques are used to remove particles of differing size as shown in Figure 1.

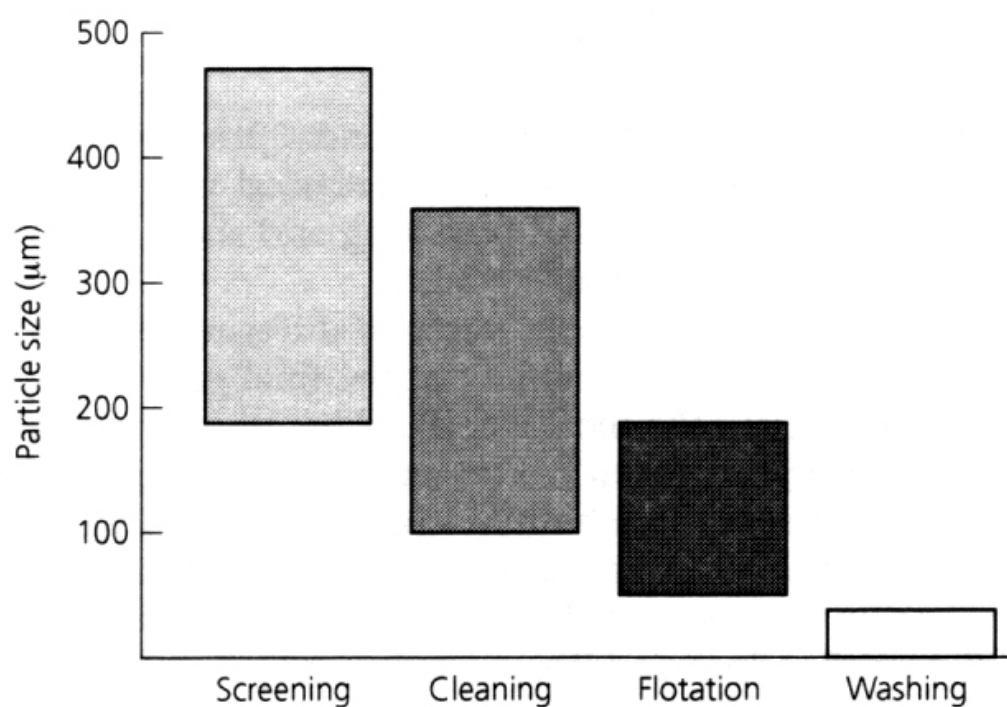


Figure 1. Particle size ranges and separation techniques

Screening

Contraries of sizes from about 200μm diameter and upwards are removed by screening. Figure 2 shows the principles of screening where pulp is passed down the screen in a circular motion and accepted fibre passes through the mesh while rejects are collected at the bottom. One disadvantage of this method is that the slurry thickens towards the bottom of the basket and the efficiency drops to such an extent that only the top part of the screen is functional.

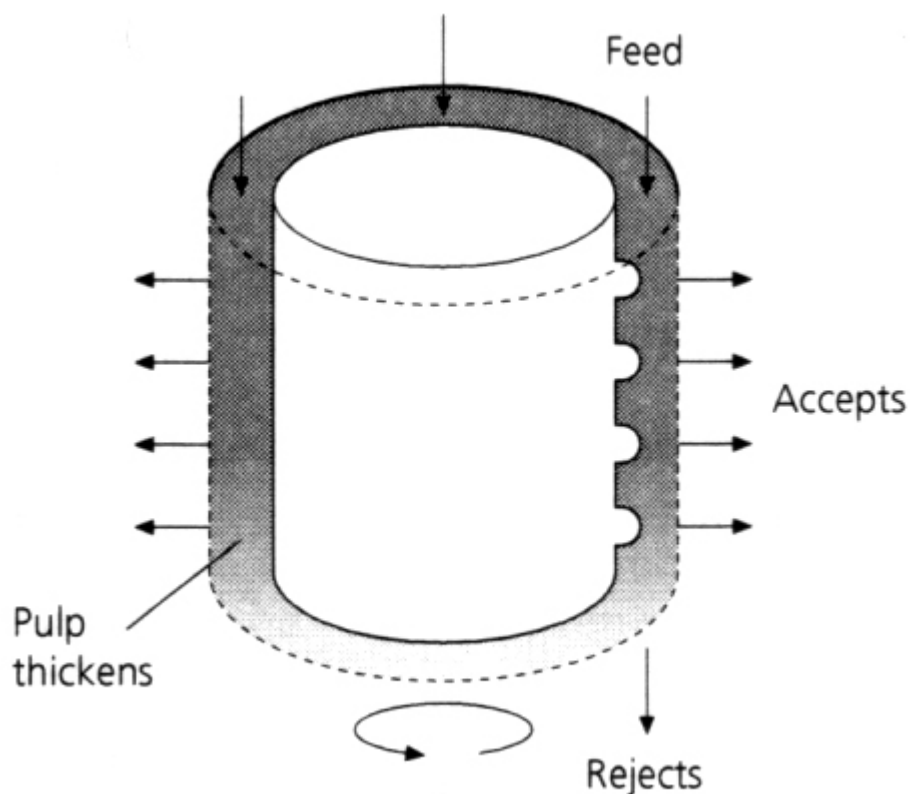


Figure 2. Diagram showing the principle of screening, where pulp is passed down the screen in a circular motion.

Cleaning

Particles in the size range 100–350 μ m are not all removed by the larger screening slits. Such debris includes sand, grit and larger ink particles such as flakes of UV-cured inks and varnishes as well as large laser ink particles. The slurry is spun around the inside of a cleaner in much the same way as a spin drier, see Figure 3. The lower density water and fibre are thrown to the outer wall of the collector while the more dense particles accumulate at the centre. The conical design of the centrifuge propels the slurry downwards and the separated debris is collected at the bottom centre outlet.

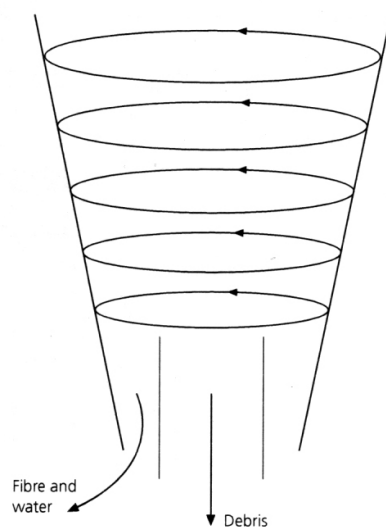


Figure 3. Centrifugal cleaning action

Flotation

The basic principle of particle removal by flotation involves blowing air bubbles into the pulp slurry. These bubbles attach themselves to the ink particles and carry them to the surface where they are removed as a foam. A chemical surfactant must be used to persuade the hydrophobic ink particles to attach themselves to the walls of the water-air bubbles. The size of the ink particles that can be removed by flotation bubbles is limited to between 50–150µm. However, the size of the air bubbles introduced into the slurry determines the efficiency of particle removal.

Since flotation is at the heart of the de-inking process considerable effort has gone into optimising the efficiency of the flotation chamber. The greater the volume of air that can be introduced into the slurry, the greater the number of bubble-ink particle collisions that can occur. It is however important to avoid creating turbulence in the slurry since this causes remixing of the ink with the fibre. The common solution has been to use low volumes of air (about 20% by volume) and increase the number of flotation cells. Earlier de-inking plants employed banks of up to six flotation chambers. More recently higher rates of air have been introduced that permit flotation removal to occur in one large chamber, see Figure 4.

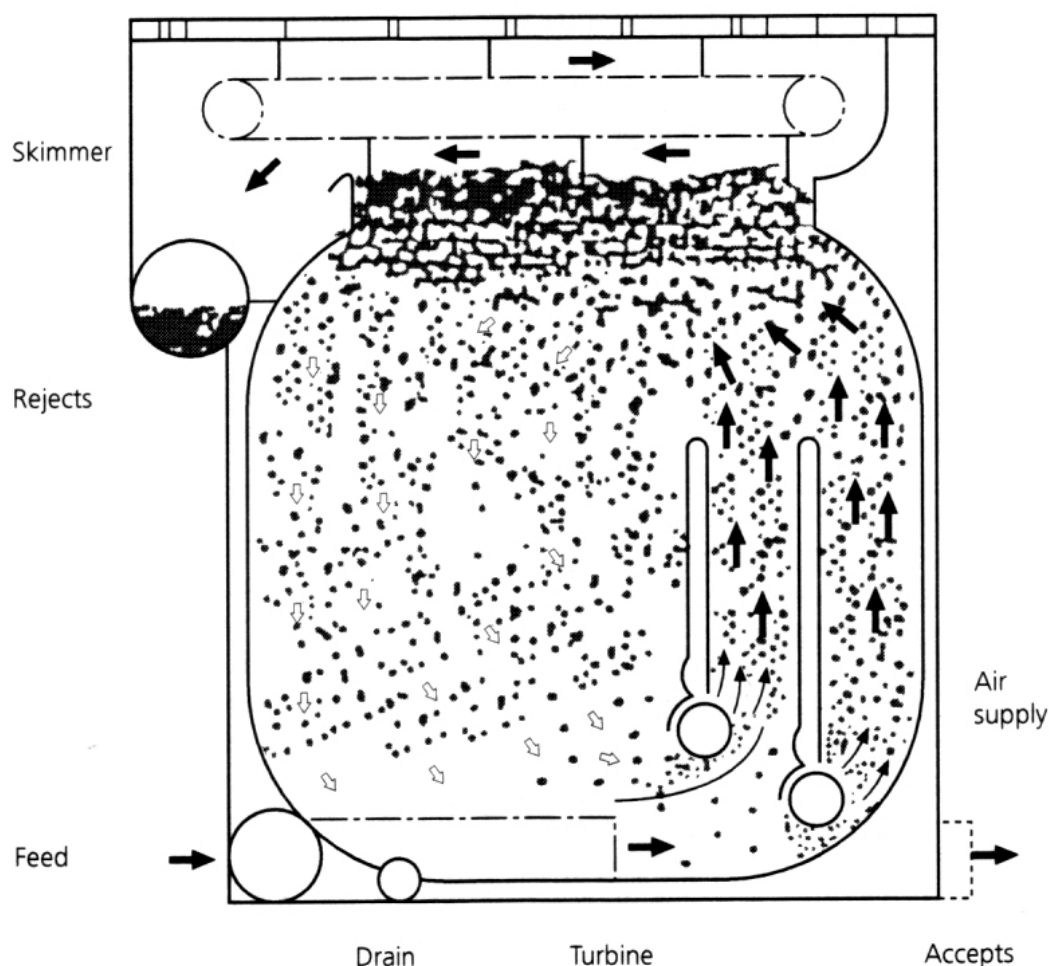


Figure 4. Schematic diagram of the Thermo Black Clawson/IIM flotator featuring high rates of air introduction

Washing

Washing technology was developed during the 1950s and 1960s. Washing does not remove larger particles but it is a very efficient technique for removing particles in the size range of 10µm and smaller. Washing requires the use of very large quantities of water and this can make the technique uneconomic. Additionally legislation demands that water is returned to its source at least as clean as when it was drawn off. This creates an enormous water-recycling task that not only requires the removal of ink particles and fillers but also the chemicals added during pulping and flotation. For this reason, washing is banned in some European countries.

There are various types of washers such as screw thickeners and side hill screens. The Black Clawson DNT washer (Figure 5) utilises a continuous wire mesh loop that travels at high speed around two rollers. A low consistency slurry (1–2% pulp in water) is fed into the inside of the moving mesh. Water is thrown out through the mesh and the pulp thickens on the first roll and is doctored off at the second roll.

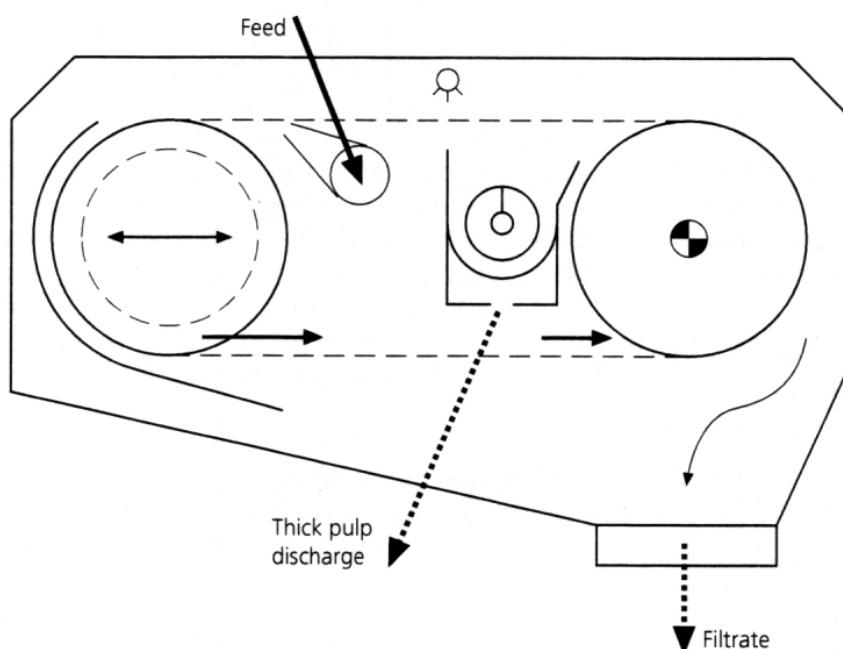


Figure 5. Schematic diagram of the Black Clawson DNT washer

The advantages claimed for this type of washer is the high rate of water separation, giving a pulp with discharge consistency of between 10 and 14%.

De-inking plant functions

Figure 6 shows a schematic arrangement of a de-inking plant based on the installation at Aylesford Newsprint in the UK. The main features of the plant include:

Pulper (continuous drum) where pulping is carried out at a consistency of 15–16% using pre-heated water at 45°C and de-inking chemicals. The drum rotates at 17rpm and baffles lift and drop the wastepaper in a gentle action which separates the fibres. Half way along the drum, water is sprayed into the mix, diluting it to a consistency of 3.5%. The intention is to remove plastic coatings and hot melt adhesives before they reach the hotter stages of the process, therefore the temperature must not exceed 45°C or these materials will soften.

Prescreening and cleaning, here larger contraries are removed. The lower section of this unit is a centrifugal cleaner which removes pins, staples and paper clips. The slurry is still at a consistency of 3.5% passes through the dcreening basket whose holes are 1-6mm in diameter.

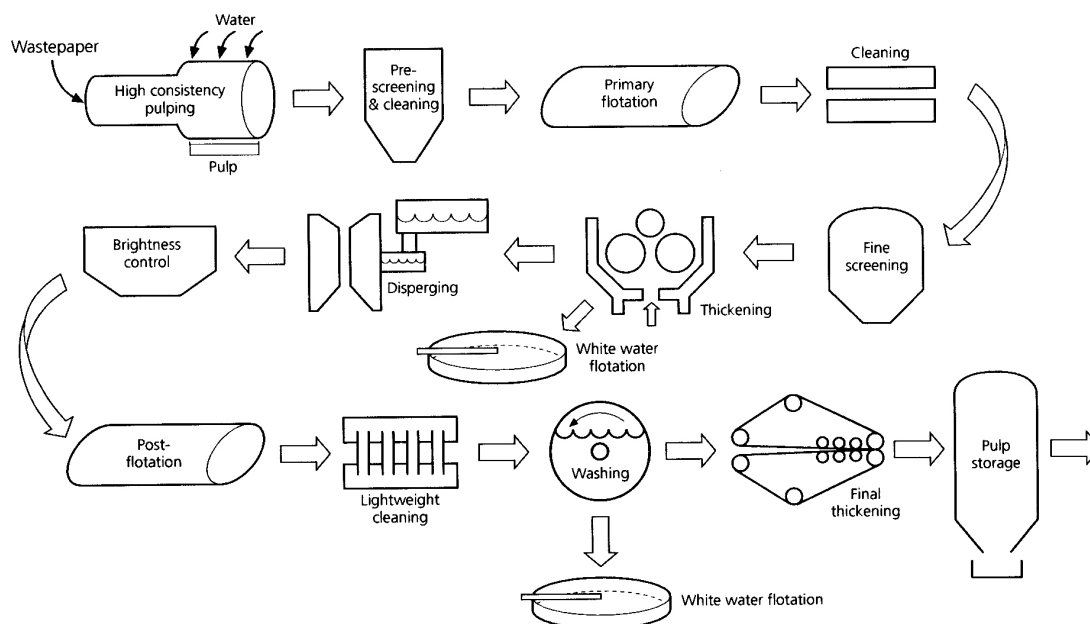


Figure 6. De-inking plant arrangement

Primary flotation is carried out at a 1.2% consistency and at a pH of 10.

Cleaning is where large UV-cured ink and varnish specks are removed along with toner particles.

Fine screening is primarily used to remove stickies. These are derived mainly from pressure-sensitive polyacrylates used in 'peel and seal' labels, envelopes and tapes as well as polyisoprene from self-seal envelopes. Other sources of stickies are hot melt and PVA perfect binding adhesives. A screen slot width of 0.15mm is used.

Thickening is the process whereby the stock is thickened from 1 to 8% at 90°C using a disc filter and then from 8 to 30% by passing through a twin-roll press. Thickening is carried out as the stock must be at the higher consistency for the latter stages, however, it does permit the removal of some smaller ink particles which are flocculated to a flotatable size.

Dispersing is where the size of remaining contaminants is reduced to facilitate their removal.

Brightness control involves the high consistency stock being bleached with hydrogen peroxide at a temperature of 90°C.

Postflotation is where dispersed inks, varnishes and the remaining fillers are removed. In order to remove water-based flexo inks at this stage the pH is reduced from alkaline to acid or neutral condition. Brightening of the pulp also occurs due to acid shock. The consistency is reduced to 1.2% to facilitate flotation.

Lightweight cleaning, here cleaners are designed to remove lightweight contaminants along with any colloidal sized particles resulting from the acid shock.

Washing removes the remaining colloidal sized particles and 'molecular' flexo inks.

Thickening and storage, here the stock is finally thickened to between 4–12% consistency before being stored, ready for use on the papermaking machine.

De-inking chemistry

Chemistry is involved at most stages in the recycling of wastepaper, in particular pulping, flotation, washing, deposit control and water clarification. Some of the chemicals employed are simple and well known such as sodium hydroxide or caustic soda (NaOH); others are quite complex such as surfactants and clarification polymers. The principle chemicals used in de-inking are shown in Table 1.

Chemical	Application
Sodium hydroxide	pulper, bleaching
Sodium silicate	pulper, bleaching
Chelating agents	pulper, bleaching
Hydrogen peroxide	pulper, bleaching
Surfactants	pulper, flotation, washing
Collector chemicals	pulper, flotation
Agglomeration chemicals	pulper, cleaners
Calcium chloride	flotation
Dispersants	washing, stock preparation
Sodium hypochlorite	bleaching
Sodium hydrosulphite	bleaching
Formamidine sulphinic acid	bleaching
Contaminant control	pulper, storage, stock preparation
Clarification polymers	clarification

Table 1. Principle de-inking chemicals (after Ferguson 1992)

In the pulper, chemistry plays a role in fibre swelling, ink removal, wetting of ink particles, flocculation, agglomeration and oxidation/reduction of chromophores. Sodium silicate (Na_2SiO_3) is used to stabilise the environment of the bleaching agent hydrogen peroxide. It also prevents redeposition of ink particles and has a high pH which assists the role of the sodium hydroxide. Sodium hydroxide assists in fibre swelling and increases fibre flexibility that helps to remove the ink. However, in newsprint furnishes, it causes yellowing of the stock (alkali darkening) by reacting with lignins in the mechanical wood content.

Table 2 shows a typical formulation for wood containing old newsprint (ONP) and wood free pulps.

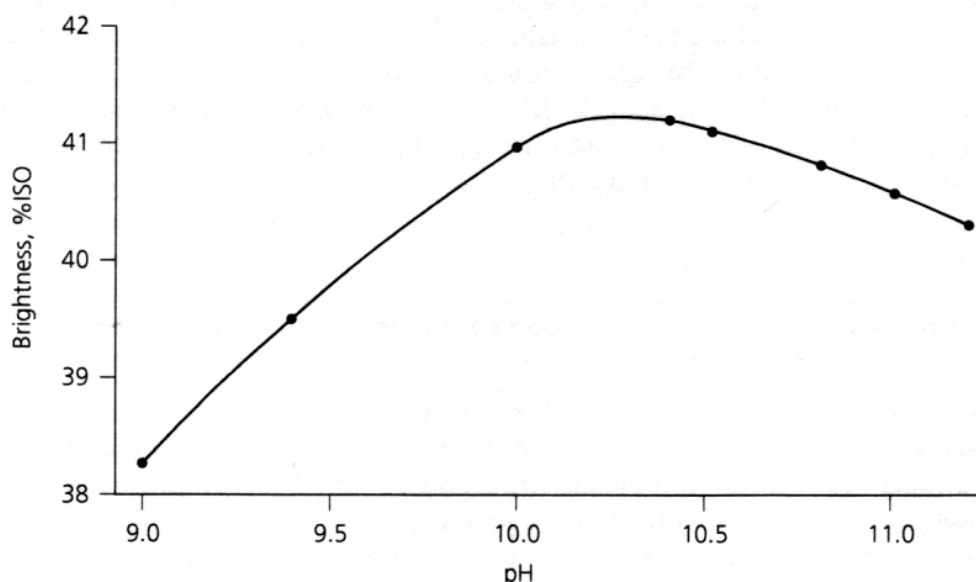
Sodium hydroxide is added to the pulper stock to adjust the pH to a value between 9.5 and 11.0. The cellulose fibres take up water and swell. During this process the fibres become more flexible and coupled with the flexing action imparted by the pulper motion assists in the removal of ink. The alkali has a second function, to saponify or hydrolyse the ink resins back to their constituent components. The resin is thus broken down, enabling the pigment to separate from the fibre.

However, the addition of sodium hydroxide in the pulper can have a detrimental effect, namely that of alkali darkening.

Chemical/condition	Wood containing	Wood free
Chelant	0.15 – 0.4%	-
Sodium silicate	1.0 – 3.0%	-
Sodium hydroxide	0.8 – 1.5%	1.0 – 1.5%
Hydrogen peroxide	0.5 – 2.0%	-
Surfactant/collector	0.25 – 1.5%	0.25 – 1.5%
Temperature	45 – 55°C	50 – 60°C
pH	9.5 – 10.5	10.0 – 11.0
Consistency	5 – 15%	5 – 15%
Time	4 – 60 min	4 – 60 min

Table 2. Typical pulper chemistry (after Ferguson 1992)

Figure 7 shows the influence of pH on the pulp brightness of a typical old newsprint / old magazine (ONP/OMG) furnish. As the pH increases from pH 9.0 to 10.2 the pulp brightness increases due to the effects of fibre swelling and saponification.

**Figure 7. The effect of pH on pulper brightness, 70:30 ONP/OMG furnish**

Above a pH of 10.2 the formation of chromophores in residual lignins reduce the brightness gains. This is supported by data showing the variation of light absorption at 450nm against pH changes in lignin, see Figure 8.

Although alkali darkening occurs in mechanical wood pulps for pH values above 10.2, in wood free pulps a pH of 11.0 can be used without evidence of yellowing.

Another pH dependent effect that alters the brightness of the pulp is that known as acid shock. If the pH of the post-flotation stock is reduced from 8.5 to 4.5, a significant gain in optical brightness occurs, see Figure 9. This may be explained by the precipitation or agglomeration of colloidal ink particles and stickies that are too small to be separated in the flotation chamber. Also, there will be a reduction in the number of chromophores contributing to alkali darkening.

As a result of alkali darkening it is necessary to bleach the slurry. Hydrogen peroxide (H_2O_2) has generally replaced the chlorine compounds that were used to bleach pulp fibre.

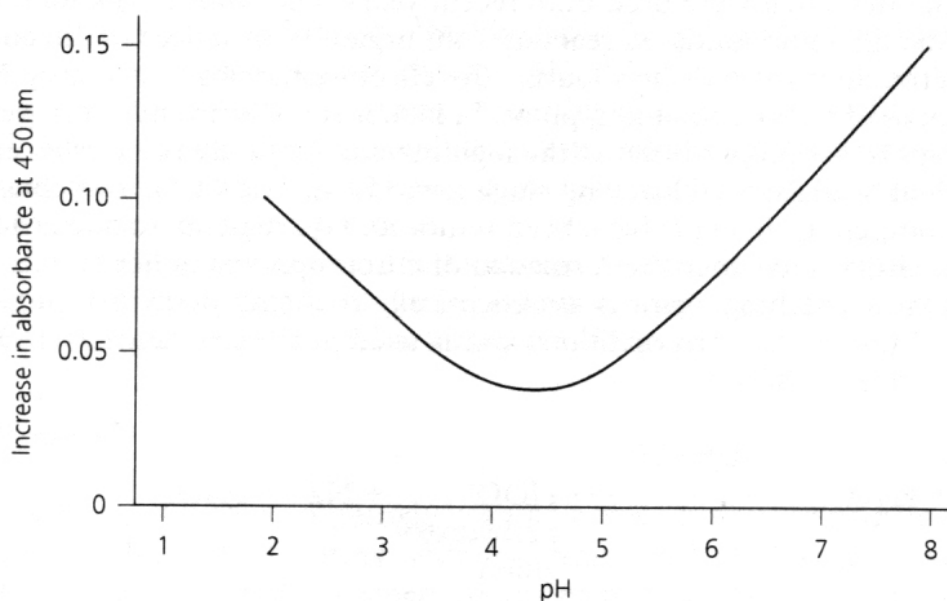


Figure 8. The effect of pH on colour formation in lignin indicated by changes in light absorption at 450nm

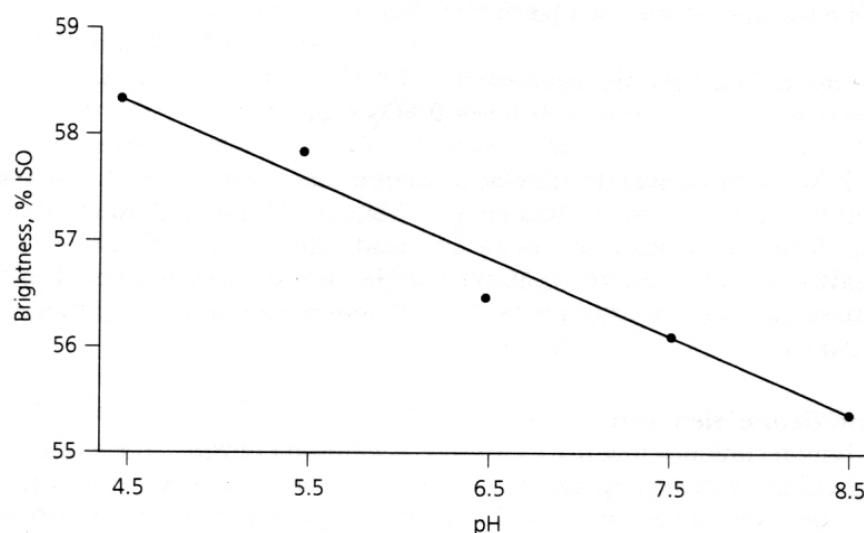
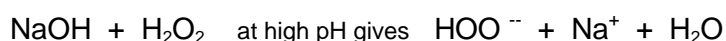


Figure 9. Acid shock: the variation of post-flotation brightness with pH

The active bleaching agent is the chemically reducing perhydroxy anion. This is only produced alkaline conditions and is used in the pH range 10.0 – 11.5 at temperatures between 40–80°C:



It has been found that peroxide bleaching at higher pulp consistencies leads to increased brightness than for medium consistencies. Thus consistencies up to 30% are used in hydrogen peroxide bleaching. The effectiveness of hydrogen peroxide bleaching is reduced by the presence of metal ions such as manganese, copper and iron. These can be present in wastepapers printed with particular magazine litho inks containing auto-oxidation driers. Other bleaching techniques that use oxidative systems involve oxygen and ozone. These strong oxidative bleaching agents can only be used where little or no mechanical wood fibre is present in the wastepaper furnish. The highest brightnesses are obtained by using a two-stage process – ozone followed

by hydrogen peroxide. The decomposition of hydrogen peroxide can be reduced by stabilising its environment using sodium silicate and a chelating agent such as pentasodium diethylenetriaminepentaacetate (DTPA), ethylenediaminetetraacetic acid (EDTA) or the sodium salt solution of diethylenetriaminepentamethylene phosphoric acid (DTPMP). However many countries have banned the use of DTPA and EDTA due to fears of adverse effects on aquatic life. Magnesium sulphate (MgSO_4) can be used as an alternative stabilising agent in virgin pulps and is now being in de-inking applications. Magnesium sulphate has been shown to have greater activity if used in conjunction with sodium silicate, where the resultant magnesium silicate is thought to deactivate the metal ions.

Sodium silicate (Na_2SiO_3) performs two functions in the de-inking pulper. As well as stabilising the peroxide environment it prevents detached ink particles from redepositing on the de-inked fibre through its ink-dispersant action. The ink particles are emulsified by the colloidal silicate particles and are thus prevented from sticking back onto the fibre.

To ensure effective de-inking it is necessary not only to remove the ink from the fibre but also to wet the detached ink particles so that they may be dispersed and prevented from redepositing onto the fibre prior to removal. All these processes require control of the surface properties of the dispersed media by the use of surfactants. Surfactant is the term that describes the actions of dispersants, collectors, wetting agents, dispellers and anti-redispersion aids. Common de-inking surfactants include those based on ethylene oxide/propylene oxide copolymers (Eo/Po). In these molecules, ethyleneoxide is the hydrophilic end and the propylene oxide is the hydrophobic end, see Figure 10.

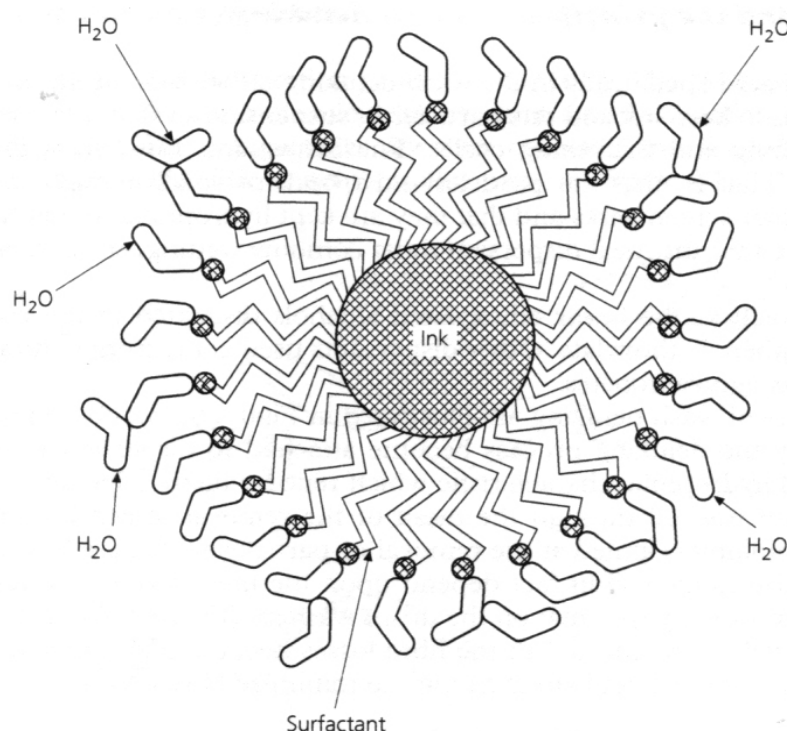


Figure 10. Surfactant micelle formation. The polar end of the surfactant molecule attaches to water, the non-polar end attaches to the ink particle. An emulsion is formed of the two components.

Dispersants are used specifically in wash de-inking. Their function is to keep ink and dirt particles in suspension so that they can be removed during the washing and thickening cycles.

The dispersants used include linear ethoxylated alcohols, nonylphenol ethoxylate or naturally occurring lignosulphonates. The principles of wash de-inking are illustrated in Figure 11.

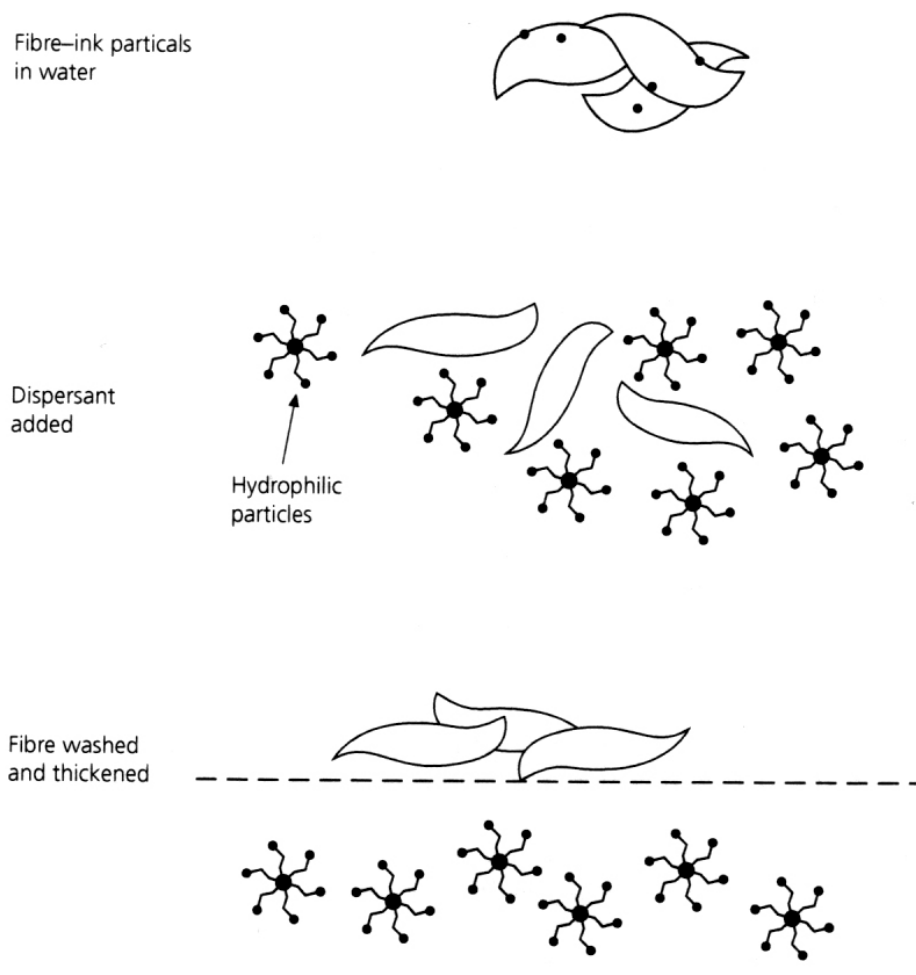


Figure 11. The principle of wash de-inking

The hydrophobic ink particles removed during the de-inking process become attached to dispersant molecules which renders them dispersible in water. The particles are then washed through the mesh of the removal screen, Wash de-inking is aimed at the removal of particles which are less than 10µm in diameter.

Collector chemicals enable the flotation process to function. The hydrophobic ink particles attach themselves to a collector molecule, which in turn attaches itself to an air bubble in the flotation chamber. Collector chemicals can be added just before the flotation stage, they include long-chain fatty acid soaps such as stearic, oleic, palmitic, linoleic or palmitoleic acids. These soluble sodium soaps must be converted into insoluble calcium soaps in order to effectively collect ink particles. The principle of flotation de-inking is illustrated in Figure 12.

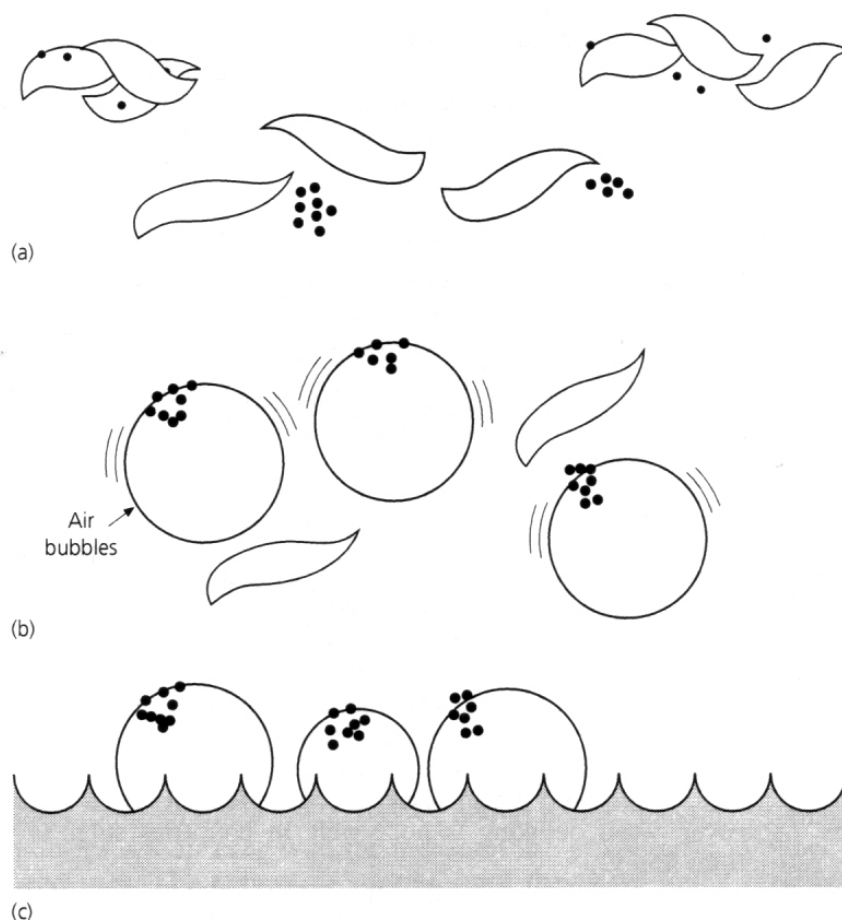


Figure 12. The principle of flotation de-inking: (a) added dispersant separate hydrophobic ink particles; (b) added collector attaches air bubbles to ink particles; (c) bubbles rise and are collected as a foam

Difficult to de-ink papers

Although conventional lithographic, flexographic, gravure and screen process inks have traditionally been removed from pulp slurries by alkaline treatments followed by simple flotation and washing techniques. The inks used in these processes usually break down with comparative ease in alkaline recycling environments and produce detached ink particles which lie within the particle size range required for flotation; that is, between 20 and 150 μm in diameter. Ink particles having diameters below 20 μm may be removed by washing. Those particles having size ranges in excess of 150 μm are removed by mesh screening and centrifugal separation. Failure to remove the larger ink particles results in unsightly dark or coloured flakes in the recycled pulp. Smaller particles which are not floated or washed from the pulp, whilst not visible to the naked eye, reduce the whiteness and printing dynamic range of the paper.

However water-based flexo inks present a particular problem to the de-inking process. The reason is that the particle size of these water-based inks are in the range 0.2 – 1.0 μm after repulping, and are too small for removal by flotation. The inks are hydrophilic and cannot be agglomerated. Although the particle size range is small, concentrations above 6–10% cause noticeable loss in pulp brightness. They could be removed by washing but that would require high volumes of water that in turn would present water clarification problems.

Other problems are found with the newer toner-based and UV-cured inks, the difficulties arise from their physical and chemical compositions that may be more complex than conventional inks (Carre and Mangin 2002, Clinkunbroomer 2003, Schmitz and Fischer 2004). The toners used in electrophotographic digital inks and photocopier systems present dual problems. Firstly, because they are heat fused to the paper, they tend to form continuous films that are uniformly strong across their areas. When detached from the paper fibres they form large platelets. These platelets are flexible and are able to flex through the conventional screens used to separate the large contaminants present in recycled slurries. Because their densities are close to that of water, centrifugal separation is equally ineffective in separating them. Above 150µm, they are too large to be separated by flotation.

The alternatives are to physically segregate these types of print or to find new ways of dealing with them; both are expensive. Conventional de-inking plants have introduced dispersers or 'dispergers' which seek to reduce their size by gentle grinding. These dispersers break down the toner particles by mechanical kneading of a 35% slurry. The high consistency pulp increases the fibre-to-fibre contact and reduces its damaging contact with the metal blades. Nevertheless, the mechanical action still introduces some breaking of the fibres, resulting in losses of the fibre from the pulp. Secondly, the fused toners are resistant to the alkaline environment used in conventional de-inking plants which makes it difficult to detach them from the paper fibres.

UV-cured inks form extremely tough films which bond tenaciously to cellulose fibres. They too break down into large platelets and may even separate as complete continuous films. Moreover, they are extremely difficult to detach from paper fibres resulting in wasteful loss of fibre. These factors, more than any other, have fostered an interest in ultrasound as a means of de-inking paper printed with new ink formulations arising from developments in printing technologies. The problem is one that is growing with the increasing volumes of paper being printed with these formulations. It has recently been reported that seven million tons per annum are currently being printed using digital printing technologies alone, a figure that is rising sharply with their increasing use.

Application of ultrasound

As a result of the introduction of these new inks that resist conventional de-inking processes there has been a revival of interest in the use of ultrasound to assist in the de-inking process (Thompson and Manning 2005).

Thompson et.al. (2000) studied the de-inking of toner printed mixed office waste (MOW) using 20kHz ultrasound at an electrical input energy of 1500W. Pulps were prepared in a laboratory disintegrator. They studied the effects of exposure time over a temperature range of 35-80°C at neutral pH. Particle size distributions were measured from hand-sheets prepared from unwashed and washed sonicated pulps using image analysis. Particle size ranges present in the filtrates were also examined. They found that temperature had little or no effect on particle size distribution following de-fibring in the laboratory disintegrator, see Figure 13.



Figure 13. Toner particles attached to fibres after disintegration but prior to sonication

However, temperature did have an effect on particle breakdown by ultrasound. Larger numbers of particle were produced at temperatures well below the softening point which was attributed to greater brittleness of the toner at lower temperatures, see Figure 14. At higher temperatures closer to the softening point, greater proportions of larger particles were produced, findings which accord with those of Gerber and Scott (1995). Furthermore, it was found that a combination of higher temperature and increased exposure time considerably enhanced the detachment of ink particles from fibres. This was evidenced by comparing the image analyses of washed and unwashed handsheets as well as particle size analyses of the filtrates. The suggested reason was that detachment was assisted by softening of toner and fibre, together with fibre swelling which occurred at high temperatures.

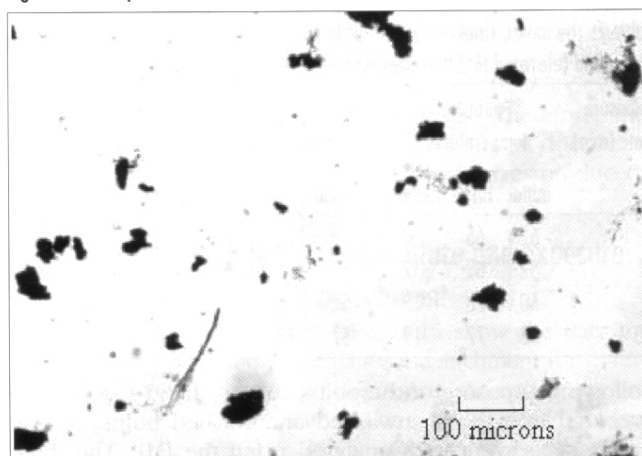


Figure 14. Toner particles detached from fibres after 10 minutes sonication

Different toner types demonstrate different values for the work of cohesion between fused toner particles. The highest value for commonly used toners is 20.35mJm^{-2} . On the other hand, values for the works of adhesion for three different toner formulations applied to a variety of base papers has been found to range from 41.2 to 62.4mJm^{-2} . Thus the energy required to break down the forces of cohesion between toner particles is considerably less than that required to overcome the forces of adhesion between toner and paper fibre. This supports the evidence from Thompson et al.

(2000) that fused toner particles are first broken down before being detached from fibre on exposure to ultrasound.

Manning and Thompson (2004) also found that exposure of pulps printed with UV-curing inks to high intensity ultrasound causes breakdown of the ink film under neutral pH conditions. This was demonstrated for both solid and half-tone printings, although it was found that the smaller the printed half-tone dot the less effective was the ultrasound in breaking them down. Some of their findings are shown in Tables 3 and 4.

Table 3. Particle size distributions found on hand sheets from 75% unwashed samples

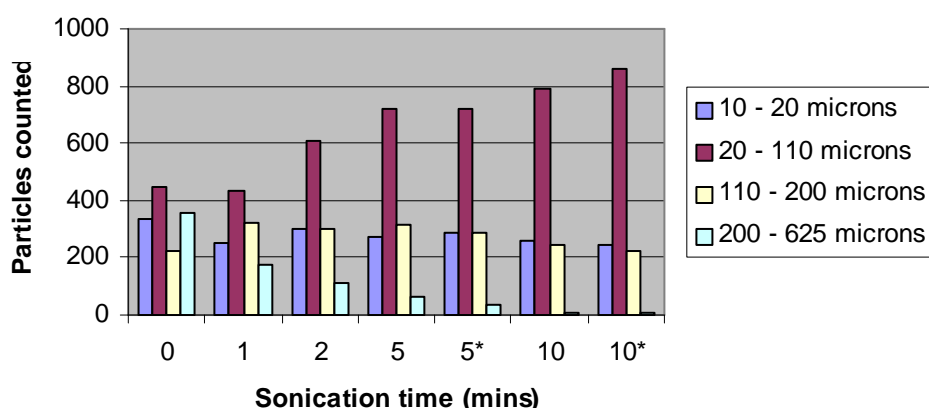
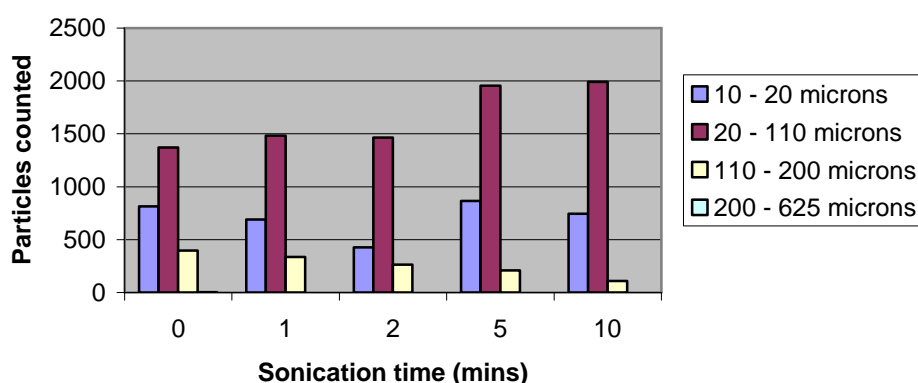


Table 4. Particle size distributions found on hand sheets from 20% unwashed samples



Concern has been expressed that the polymer films created by the Indigo Electroink pose serious problems for de-inking because they produce great quantities of ink particles that are in excess of 150µm diameter and may not be removed by screens because the particles are too soft, thin and flexible; Indigo inks have been described as 'unde-inkable' (Carre and Mangin 2002). Furthermore, in common with conventional lithographic printing, the difficulty appears to increase with ageing of the prints.

Indigo printing differs from other forms of electrostatic transfer digital printing in that it is an offset process which involves the transfer of a liquid toner suspension, having the trade name Electroink, from the imaging drum to a heated offsetting blanket and thence to the substrate. The advantages claimed for the blanket are the same as for conventional lithography: it protects the surface of the imaging drum from wear and allows a range of substrates to be printed (Williams 2004). Indigo's claimed advantage over dry toner processes lies in the smaller sizes of toner particles used; these are between 1 and 2 μm . Dry toners having this size range produce smokes which are difficult to control. However, the liquid medium in which Electroink particles are dispersed overcomes this problem with the result that finer resolutions and higher print quality may be achieved.

Little information has been released about the composition of Indigo inks but it has been suggested that they contain a mineral oil varnish and pigments similar to lithographic inks. The toner system comprises pigmented thermoplastic polymer particles dispersed in a non-polar solvent. According to the US Patent, at temperatures below 40°C the thermoplastic polymer is insoluble in the carrier oil. Above 50°C, the polymer is able to solvate in the carrier liquid and above 70°C the polymer particles melt and fuse (Landa et.al. 1988).

During the printing process the liquid toner is transferred to the blanket that is heated to 100°C. This causes the suspended toner particles to melt and fuse together, forming a 'hot adhesive liquid plastic'. When the ink contacts the relatively cool substrate it solidifies, sticks to it and is stripped off the blanket, leaving no residue behind. Thus, unlike conventional inks, the Electroink transfers completely from the blanket, without splitting of the ink film, which allows a new and completely different image to be printed on every new cycle.

Although Indigo digital presses can print on a wide range of substrates, problems were initially experienced with printing on paper because the liquid toner did not always adhere uniformly to it, causing patchy prints. To overcome this problem, Indigo developed a coating that they called 'Sapphire' and which is applied to the paper as a pre-treatment before printing. Based on polyethylene imine (PEI), the coating helps the ink to bond to the paper. However, the PEI has a tendency to yellow on storage and also the paper is relatively expensive. Eastern Paper has recently introduced a new paper which does not require pre-treatment and which uses patented technology to improve adhesion; it is also colour stable. The higher cost of these papers has resulted in many printers electing for cheaper conventional coated and uncoated papers at the possible expense of print quality.

Since current world consumption of paper for digital printing is about 7.5 million tons per annum which represents about 7.5% of the worldwide printing consumption, the de-inkability of digital prints has become an issue for recyclers. The recently introduced HP Indigo 5000 has transformed digital printing into the mainstream of commercial print with the ability to produce one million impressions per month. The potential for large quantities of Indigo printings to enter the recycling chain is therefore significant.

Fricker et.al. explored the efficiency of ultrasound in the de-inking and size reduction on Indigo digital prints, two types of image and two types of substrate were selected for comparison (Fricker et.al.2006). The first image comprised a combination of graphic images and text, since these are the most common types of printed matter. The second comprised solid areas of ink since these were considered to be potentially the most problematic to break down. In both cases, black ink was used to simplify ink particle counting.

The two papers chosen were 115gsm Mediaprint Silk and Indigo's Sapphire coated paper. Sapphire was chosen because this is the preferred choice for Indigo printing for reasons already discussed. The Mediaprint Silk was chosen because it is a cheaper paper of the type often used by economically minded printers. In fact, the base papers are the same for both types and only the coatings differ. However, the coatings play a major part in ink adhesion and hence the ease of de-inking and so may be considered a major variable. Strength of adhesion of the coating to the base paper is also an important factor in the removal of ink. All prints were made using an Indigo 3000 press.

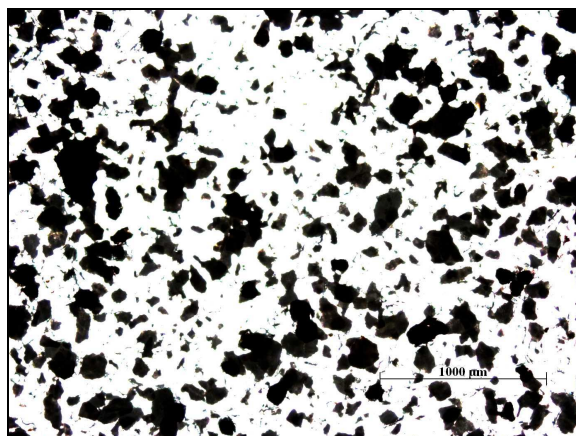


Figure 15a. Photomicrograph of handsheet from unwashed pulp after 0 minutes sonication

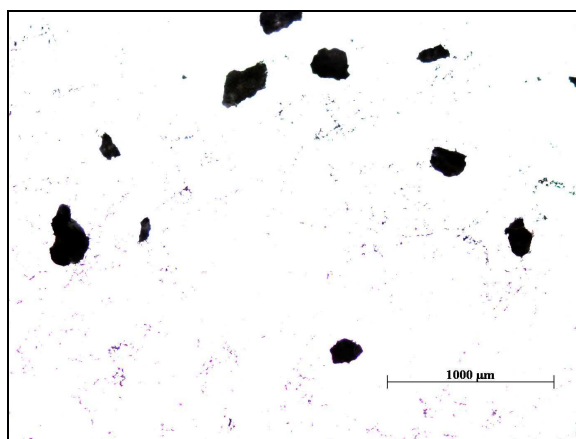


Figure 15b. Photomicrograph of handsheet from 10 minute washed pulp after 0 minutes sonication

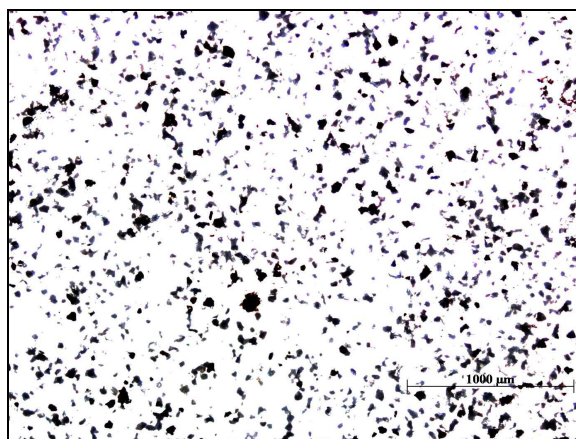


Figure 15c. Photomicrograph of handsheet from unwashed pulp after 20 minutes sonication

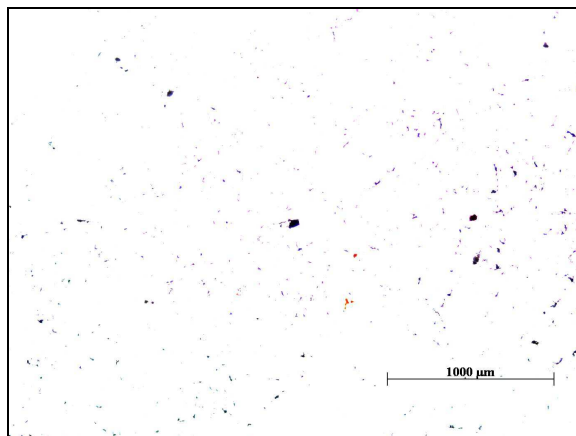


Figure 15d. Photomicrograph of handsheet from 10 minute washed pulp after 20 minutes sonication

Figures 15a to 15d show photomicrographs of handsheets derive from Sapphire coated paper printed as solid (100%) prints. At a power density of 188kWm^{-2} , there is evidence of substantial breakdown of particles, see Figure 16. This is noticeable after 10 minutes of treatment and is significantly more pronounced after 20 minutes. This is observed for all printings on both Mediaprint Silk and Sapphire coated papers although there is some evidence that de-inking of Sapphire coated papers is more readily achieved. The higher power density rating was found to be very effective in breaking down large particles to the flotatable size range.

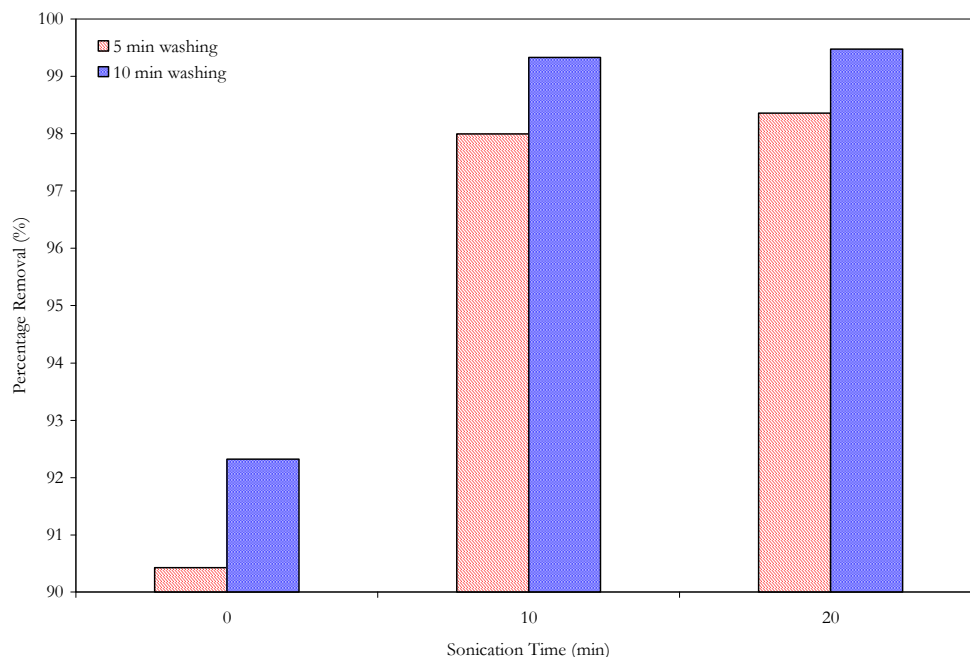


Figure 16. Ink particle removals by percentage for solid Indigo printings following zero, 10 and 20 minutes sonication at 188kWm^{-2}

Similar results were found for the text and image Indigo printings at the same power density as shown in Figure 17.

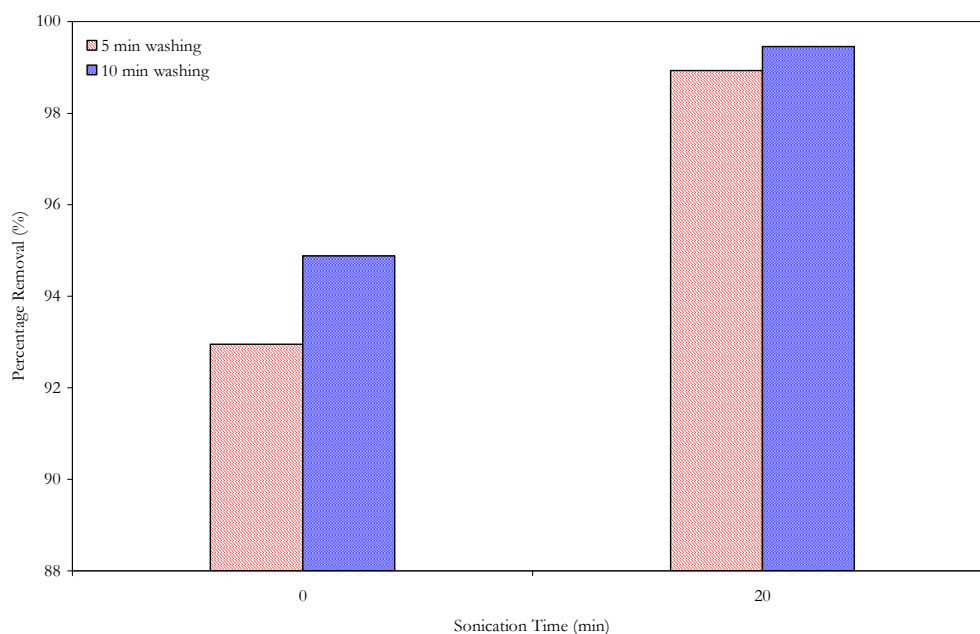


Figure 17. Ink particle removals by percentage for text and image Indigo printings following zero and 20 minutes sonication at 188kWm^{-2}

Indigo inks do not appear to be as difficult to remove as has been generally feared and can be de-inked to about 90% simply with disintegration and washing under neutral conditions. Application of ultrasound, however, removes almost 100% of the ink.

Ultrasound can be used to engineer the break down of ink particles to flotatable sizes for the de-inking process.

References

Carre B. and Mangin L. (2002), *Digital printing: a threat to the deinking industry?* PTS-CTP Deinking Symposium, Bordeaux, France, pp7-2 to 7-15.

Clinkunbroomer J. (2003), *Paper trends: no ink need apply*. Quick Printing 26(6) March pp42-43.

Fricker A., Manning A. and Thompson R. (2006), Deinking of Indigo prints using high-intensity ultrasound. Surface Coatings International Part B: Coatings Transactions, 89, B2, June, pp145-155.

Furguson L.D. (1992), *Deinking Chemistry part 1*, TAPPI Journal, July, p7

Landa B., Ben-Auraham P., Hall J. and Gibson G. (1988), *US Patent No 4794651* Dec 27th.

Manning A.N. and Thompson R.C. (2004), *De-inking of thick film UV-cured coatings using high intensity ultrasound*. Surface Coatings International Part B: Coatings Transactions, 87, B1, 1-70, February, pp22-26.

Schmitz U., Fischer A. (2004), *Recycling killer in digital clothing: digital inks cause recycling problems*. Druck Medien magazine Sept, pp34-35.

Scott W.E. and Gerber P. (1995), *Using ultrasound to deink xerographic waste*. TAPPI J. 78 (12) pp125-130.

Thompson R. (2004), *Printing Materials – Science and Technology* 2nd Edition, Pira International.

Thompson R. and Manning A. (2005), *A review of ultrasound and its applications in papermaking*. Progress in Paper Recycling, 14(2) Feb, pp26-42.

Thompson R.C., Manning A. and Lane J. (2000), *An investigation of the effect of temperature and exposure to ultrasound on the de-inking of mixed recoverable office waste*. Surface Coatings International 83, (7), pp322–328.

Williams C.H. (2004), *Electrographic Printing*. Print. Pap. Mon. vol 16 No 7 October p18.